

## ACTIVITY OF SLURRY PHASE IRON-BASED CATALYSTS FOR HYDROGENATION AND HYDROCRACKING OF MODEL SYSTEMS

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### INTRODUCTION

Slurry phase catalysts have been shown to be very active for coal liquefaction. Pellegrino and Curtis (1989) compared the activity of three different types of molybdenum catalysts: an oil-soluble molybdenum naphthenate, a presulfided molybdenum on alumina, and a precipitated  $\text{MoS}_2$  catalyst. The catalyst generated *in situ* from molybdenum naphthenate was the most active in terms of hydrogenation and heteroatom removal as well as showing the highest coal conversion and product upgrading. Kim and Curtis (1990) evaluated catalyst precursors of molybdenum, nickel, and vanadium for their activity in coprocessing of coal with resid. The activity of the molybdenum and nickel precursors for coal conversion and oil production was high while that for the vanadium was low.

Comparisons of the catalytic activities of iron and molybdenum catalysts used in reactions of model coal molecules showed that  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}(\text{CO})_5\text{-S}$  had high catalytic activity for hydrogenation of aromatic species (Suzuki et al., 1989). However,  $\text{Mo}(\text{CO})_6\text{-S}$  more strongly promoted hydrogenation of polyaromatic compounds as well as hydrogenation of some phenyl carbon bonds. The effect of dispersion methods had also been examined using iron catalysts in which an iron oxide ( $\text{FeOOH}$ ) precursor was dispersed onto the solid coal matrix (Cugini et al., 1991). Other iron systems, such as  $\text{Fe}_2\text{O}_3$  dispersed on carbon black, iron incorporated into coal by impregnating with  $\text{FeCl}_3$  and iron incorporated into lignite by cation exchange with a sulfated  $\text{Fe}_2\text{O}_3$ , have been used as finely dispersed catalysts for coal liquefaction and characterized by Mössbauer and XAFS spectroscopy (Huffman et al., 1991).

Finely divided iron (III) oxides and iron oxyhydroxides modified with either ( $\text{SO}_4^{2-}$ ) or molybdate ( $\text{MoO}_4^{2-}$ ) anions used in coal liquefaction have shown increased coal conversion and selectivities to n-pentane soluble products (Pradhan et al., 1991). A bimetallic catalyst,  $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$  that consisted of 50 ppm Mo and 3500 ppm Fe, was active for coal conversion with a selectivity for oil. The effect of the pyrite to pyrrhotite ratio produced from ferric sulfide as a precursor on coal liquefaction has also been studied. A definite effect of intermediate stoichiometry of the ratio was observed on the selectivity to lighter products at higher liquefaction temperatures (Stansberry et al., 1991).

In this investigation, the effect of slurry phase iron catalysts on hydrogenation and hydrocracking reactions of model coal species was investigated. The areas investigated included (1) the effect of iron complex type on hydrogenation of pyrene and on hydrocracking of alkyl substituted naphthalenes; (2) the effect of different dispersion methods on catalytic activity of iron-based slurry catalyst precursors; and (3) the effect of combining iron with molybdenum slurry phase catalyst precursors on catalytic activity during the hydrogenation of pyrene.

## EXPERIMENTAL

The experimental reaction methods used for dispersing the catalyst precursors were (1) *in situ* where the catalyst precursor was added directly to the reaction system and reacted in the presence or absence of sulfur; (2) *ex situ* where the catalyst precursor reacted in the presence of the model compound was reclaimed and used in a second reaction and (3) two stages where the catalyst precursor was added to hexadecane, hydrogen, and sulfur and reacted for 30 min, then the model species was introduced into the reactor along with hydrogen and reacted for another 30 min.

**Pyrene Hydrogenation Reactions.** Iron slurry phase catalyst precursors were compared and utilized the *in situ* reaction method; molybdenum naphthenate was also used for comparison. The iron catalyst obtained *in situ* was generated by introducing the catalyst precursor at a level of 900 to 1100 ppm metal directly into the reaction system of 2 wt% pyrene in hexadecane. The reactants were charged into a 20 cm<sup>3</sup> stainless steel tubular microreactor and the reactions were conducted at 380 or 425°C for 30 or 60 min with a hydrogen pressure of 1250 psig at ambient temperature and an agitation rate of 550 rpm. Reactions were performed both with and without sulfur. When sulfur was present, it was introduced as elemental sulfur in a stoichiometric ratio of 3:1 sulfur to metal, presuming that either FeS<sub>2</sub> or MoS<sub>2</sub> was formed depending upon the precursor introduced.

The catalysts precursors used in the *in situ* experiments were iron (III) naphthenate, iron (III) acetylacetonate, iron (III) citrate hydrate, iron (III) 2-ethylhexanoate, iron (III) stearate, and molybdenum naphthenate for comparison. Iron (III) acetylacetonate (99% purity) was obtained from Eastman Kodak Company; iron (III) citrate hydrate (98% purity) was obtained from Aldrich Chemical Company; iron (III) 2-ethylhexanoate (8 to 11.5% Fe), iron (III) acetylacetonate (99% purity), and iron (III) stearate (9% Fe) were obtained from Strem; and the molybdenum naphthenate (6% Mo) was obtained from Shepherd Chemical. All of the catalyst precursors were used as received.

The *ex situ* catalyst was generated by collecting the catalyst solids produced during an *in situ* reaction and then drying the solids for 72 hours in a vacuum oven at 60°C. The dried solids were then introduced into the reactor containing pyrene in hexadecane solution at a level of 900-1100 ppm active metal. Hydrogen was introduced and the reaction was performed at the abovementioned conditions.

Two-stage pyrene hydrogenation reactions were performed by producing the catalyst in the first stage using a reaction system of catalyst precursor, excess sulfur, hexadecane, and a hydrogen pressure of 1250 psig at ambient temperature. After 30 min of reaction, the reactors were removed from the sandbaths, cooled, and then charged with pyrene and 1250 psig hydrogen introduced at ambient temperature. The pyrene hydrogenation reaction was then performed at 380°C for 30 min.

An analysis procedure UV-visible spectroscopy was developed for measuring the amount of organometallic complex that reacted under liquefaction conditions. The procedure developed used the metal complex dissolved in hexadecane as the reaction system. The concentration of the iron or molybdenum complex present after a given reaction time was determined by UV-visible spectroscopy. Each iron complex had to be dealt with differently in the experimental procedure because of their varying degrees of solubility in hexadecane. Iron naphthenate, iron 2-ethylhexanoate, and molybdenum naphthenate utilized hexadecane as a solvent for UV-visible spectroscopy. Iron citrate hydrate was dissolved in ethanol for analysis; iron acetylacetonate was

extracted with hot water for UV-visible analysis. For each metal complex, a calibration curve was developed using the same solvent for UV-visible analysis as was used after reaction.

The reactions using different amounts of iron and molybdenum complexes involved adding the different metal complexes *in situ* to the 2 wt% pyrene hydrogenation system. These experiments were performed at the same conditions as the previously described *in situ* reactions except that the iron and molybdenum complexes were added in weight ratios of 75:25, 50:50, and 25:75.

**Hydrocracking Reactions.** Two compounds were used as hydrocracking models: 1-methylnaphthalene and 2-hexylnaphthalene. 1-methylnaphthalene was obtained from Aldrich while 2-hexylnaphthalene was obtained from Dr. M. Farcasiu of PETC. The reaction system consisted of 2 wt% of the model compound dissolved in hexadecane. Three catalyst precursors were tested: iron naphthenate, iron stearate and molybdenum naphthenate; all of which were introduced at a level of 900 to 1100 ppm metal directly into the reaction system. Thermal baseline experiments were also performed. The reaction conditions were reaction temperatures of 380 or 425°C for 30 min with a hydrogen pressure at 1250 psig at ambient temperature and an agitation rate of 550 ppm.

**Analysis.** The reaction products obtained from the pyrene hydrogenation reactions were analyzed by gas chromatography using a Varian Model 3700 gas chromatograph equipped with FID detection and J&W DB5 30 m column. Quantitation was achieved by employing the internal standard method using p-xylene as the internal standard. The reaction products were identified comparing retention times with those of authentic compounds and by identifying unknowns by GC-mass spectrometry using VG70 EHF GC-mass spectrometer.

The product slates were determined for each reaction and the amount of hydrogenation of the aromatic determined. The percent hydrogenation is defined as the moles of hydrogen required to produce the product slate as a percentage of the moles of hydrogen required to produce the most hydrogenated liquid product. The most hydrogenated liquid product from naphthalene was considered to be decalin, from pyrene, perhydropyrene, from 1-methylnaphthalene, 1-methyldecalin and from 2-hexylnaphthalene, 2-hexyldecalin. Percent hydrocracking is defined as the mole percent of the products that have undergone hydrocracking.

## RESULTS AND DISCUSSION

**Pyrene Hydrogenation Reactions.** Of the five slurry phase catalysts tested for their activity for pyrene hydrogenation, Fe naphthenate (Fe Naph) was the most active while Fe stearate (Fe STR) showed equivalent activity at 425°C but lesser activity at 380°C (Table 1). Sulfur was required for any activity to be observed from either catalyst. The primary product obtained was dihydropyrene (DHP), the secondary products were hexahydropyrene (HHP), and small amounts of tetrahydropyrene (THP) were formed.

Of the other three slurry phase iron catalysts tested with sulfur, Fe AcAc reacted at 425°C was the only one which showed substantial pyrene hydrogenation of 9.3% and yielded the same products as Fe Naph. All of the other systems with sulfur, Fe citrate-hydrate (Fe CH) and Fe 2-ethylhexanoate (Fe 2-EH) showed limited activity for pyrene hydrogenation.

Reactions were also performed with Mo Naph with and without sulfur at 380 and 425°C for 30 min. The presence of sulfur in the reactor allowed the Mo released from Mo Naph to form finely divided MoS<sub>2</sub> which was an active catalyst for pyrene hydrogenation (Kim et al., 1989). At 380°C, without sulfur, the reaction with Mo Naph yielded 11.7% HYD with DHP

as the primary product and THP as the secondary product. At 380°C, with sulfur, the reaction with Mo Naph yielded 34.6% HYD of pyrene with HHP isomers being the primary products and a substantial amount of decahydropyrene (DCHP) being formed.

At 425°C, the reaction of Mo Naph without sulfur showed less activity for pyrene hydrogenation than did the system with sulfur. Without sulfur the %HYD of pyrene was somewhat higher at 13.8% than at 380°C which yielded 11.7%. But the reaction at higher temperature, 425°C, with sulfur gave less activity than at 380°C with sulfur. At 425°C, thermodynamics are limiting the amount of pyrene conversion allowed and, hence, lower the amounts of partially saturated compounds produced in the reaction (Ting et al., 1992).

**Concentration of Iron Complexes at Liquefaction Conditions.** The iron complexes of Fe-CH, Fe Naph, Fe AcAc, and Fe 2-EH, each with an initial concentration of 1000 ppm Fe, were reacted at 380°C with an initial hydrogen charge of 1250 psig hydrogen introduced at ambient temperature. The concentration of each iron complex was determined by measuring the absorbance at two wavelengths and comparing the absorbance reading with a calibration curve for each complex obtained with the same solvent as was used with the reaction mixture. Each of the iron complexes disappeared very quickly at liquefaction conditions. After 5 min of reaction, all of the iron complexes were decomposed; in fact, all of them except Fe Naph were decomposed after 2 min of reaction. By contrast, Mo Naph remained in solution longer; after 10 min of reaction, more than half of the Mo Naph remained. However, Mo Naph had totally decomposed after 15 min of reaction.

**Comparison of Dispersion Methods for Activity of Fe Slurry Phase Catalysts.** Three methods of dispersion *in situ*, *ex situ*, and two stage batch processing were used to test the effect of dispersion on the catalytic activity of the generated catalysts (Table 2). Comparison of Fe Naph and Mo Naph activity for pyrene hydrogenation using the *in situ* method revealed that Mo Naph resulted in nearly three times as much hydrogenation as Fe Naph. HHP was the primary product for Mo Naph while DHP was the primary product for Fe Naph. The *ex situ* method, in which the catalyst produced in an *in situ* experiment was added to pyrene hydrogenation reaction system, resulted in less activity for both Fe Naph and Mo Naph. Fe Naph did not convert any pyrene while Mo Naph yielded about half the amount of hydrogenation observed in the *in situ* reaction.

Two-stage batch reactions were performed in which the catalyst precursor was introduced into hexadecane in the first stage and then reacted in the presence of sulfur and hydrogen for 30 min at 380°C. At that point, the reaction was quenched, gas released and pyrene and a new charge of hydrogen added. The system, including pyrene, was then reacted again for 30 min. The two-stage reaction with Fe Naph yielded about 6% conversion of pyrene to DHP so that its activity was much less than that of the *in situ* generated catalyst. By contrast, the two-stage reaction with Mo Naph yielded higher pyrene hydrogenation, 40% for the two-stage compared 34.6% for the *in situ* single-stage. Hence, the catalytic activity of Mo Naph appeared to increase with the two-stage treatment while Fe Naph did not.

**Effect of Combining Iron Complexes with Mo Naphthenate on the Reaction Products from Pyrene Hydrogenation.** Reactions were performed in which the catalyst precursors of the various iron complexes were combined with Mo Naph to determine if any synergism occurred in their catalytic activity for pyrene hydrogenation (Figure 1). Reactions were performed with 1000 ppm of the iron complex, 1000 ppm of Mo Naph, and with the combinations of 750 ppm iron complex with 250 ppm Mo Naph, 500 ppm with 500 ppm, and 250 with 750 ppm, respectively.

The combination of Fe Naph and Mo Naph at 75:25 and 50:50 Fe to Mo ratio yielded increased pyrene hydrogenation compared to either Mo Naph or Fe Naph alone. These results are presented in Figure 1 along with baseline experiments using Fe Naph and Mo Naph, individually. With Fe AcAc and Fe CH, each combined with Mo Naph, increased pyrene hydrogenation was observed at the combination of 25:75 Fe to Mo compared to the Mo Naph alone. By contrast, none of the combinations of Fe 2-EH with Mo Naph yielded increased conversions. In fact, the amount of pyrene hydrogenation increased with the amount of Mo Naph added; however, the amount of pyrene hydrogenation was less with Fe 2-EH than with Mo Naph alone at equivalent concentration levels. Therefore, for some combinations of Fe complexes and Mo Naph, synergism between the two catalyst precursors occurred resulting in increased pyrene hydrogenation, while another iron complex was detrimental to pyrene hydrogenation.

**Hydrocracking Reactions Using Fe Naphthenate and Fe Stearate.** Hydrocracking reactions using 1-methylnaphthalene (1-MN) and 2-hexylnaphthalene (2-HN) were performed using Fe Naph and Fe STR. The product distributions obtained with these reactions were compared to that obtained with naphthalene (NAP) (Table 3). The primary products obtained from 1-MN as shown in Table 3 were 5,6,7,8-tetrahydro-1-methylnaphthalene (5,6,7,8-1-MN) and 1,2,3,4-tetrahydro-1-methylnaphthalene (1,2,3,4-1-MN). For all catalysts the 5,6,7,8-1-MN isomer was the preferred product. At the higher reaction temperature, both iron complexes yielded NAP as a secondary product. If 1-methyldecalin is considered the most hydrogenated product, then the iron complexes both yielded between 6 and 7% hydrogenation of 1-MN but less than 3% hydrocracking. By contrast, Mo Naph yielded substantially more hydrogenation of ~26% but no hydrocracking. The baseline reaction using NAP only yielded tetralin (TET) as a product. No hydrocracking of the aromatic rings was obtained.

The reactions of 2-HN also given in Table 3 in the presence of Fe Naph, Fe STR and Mo Naph resulted in the production of two products: 2-hexyltetralin (2-HT) and 2-ethyltetralin (2-ET). For all three catalyst precursors, 2-HT was the primary product while 2-ET was the secondary product. Of all of the catalyst precursors, Mo Naph yielded the most hydrogenation and hydrocracking.

## SUMMARY

Slurry phase iron catalysts showed varying amounts of activity for pyrene hydrogenation reactions. Fe naphthenate and Fe stearate were the most active complexes although all of the Fe complexes broke down quickly at liquefaction conditions. By comparison, at the same reaction conditions, Mo naphthenate gave higher activity for pyrene hydrogenation. The activity of the slurry phase iron catalysts for pyrene hydrogenation depended upon the ligand type, reaction temperature and sulfur addition. The dispersion method also made a substantial difference in the activity of the catalyst. Fe naphthenate yielded the most activity using the *in situ* dispersion method and the least using the *ex situ* method. By contrast, Mo naphthenate showed the most activity with the two-stage process and the least with the *ex situ* method. Combination of some iron complexes with Mo naphthenate showed marked increases in activity for pyrene hydrogenation. In particular, the combination of Fe naphthenate with Mo naphthenate yielded increased yields of hydrogenated products from pyrene. Hydrocracking reactions revealed that the iron complexes promoted a small amount of hydrocracking with 1-methylnaphthalene and more with 2-hexylnaphthalene although Mo naphthenate promoted more hydrocracking of 2-hexylnaphthalene at equivalent reaction conditions.

## NOMENCLATURE

PYR	= pyrene	Fe STR	= iron stearate
DHP	= dihydropyrene	Fe 2-EH	= iron 2-ethylhexanoate
THP	= tetrahydropyrene	Mo Naph	= molybdenum naphthenate
HHP	= hexahydropyrene	2-HN	= 2-hexylnaphthalene
DCHP	= decahydropyrene	2-HT	= 2-hexyltetralin
1-MN	= 1-methylnaphthalene	2-ET	= 2-ethyltetralin
NAP	= naphthalene	1,2,3,4-1-MN	= 1,2,3,4-tetrahydro-1-methylnaphthalene
TET	= tetralin	5,6,7,8-1-MN	= 5,6,7,8-tetrahydro-1-methylnaphthalene
Fe Naph	= iron naphthenate	%HYD	= percent hydrogenation
Fe AcAc	= iron acetylacetonate		
Fe CH	= iron citrate hydrate		

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Table 1. Activity of Iron Complexes for Pyrene Hydrogenation

Product Distribution (mol %)	Fe Naphthenate		Fe Stearate		Fe Citrate-Hydrate		Fe Acetylacetonate		Fe 2-ethyl-Hexanoate	
	380°C	425°C	380°C	425°C	380°C	425°C	380°C	425°C	380°C	425°C
3:1 S to Fe Ratio										
PYR	49.7±1.0	52.9±1.9	75.7±0.2	53.4±0.7	93.3±0.7	NP	95.6±0.7	61.6±0.6	100	90.5±0.7
DHP	32.1±0.5	29.1±0.5	18.2±0.2	26.7±0.6	6.7±0.7	NP	4.4±0.7	24.0±0.5	0	9.5±0.7
THP	2.9±0.1	3.2±0.3	0.0±0.0	3.2±0.4	0	NP	0	2.2±0.1	0	0
HHP	15.4±0.3	14.9±0.6	6.1±0.2	16.8±0.2	0	NP	0	12.3±0.2	0	0
% HYD	12.0±0.3	11.5±0.6	5.2±0.2	11.9±0.4	1.0±0.1	NP	0.6±0.1	9.3±0.1	0.0	1.4±0.1
No Sulfur										
PYR	98.2±0.1	87.9±0.2	100.0	100.0	100.0±0	NP	98.8±0.8	93.1±0.5	100	94.2±0.2
DHP	1.8±0.1	12.1±0.2	0.0	0.0	0	NP	1.2±0.8	6.9±0.5	0	5.8±0.2
% HYD	0.3±0.0	1.7±0.0	0.0	0.0	0	NP	0.2±0.0	1.0±0.1	0.0	0.8±0.0

Reaction Conditions: 900-1100 ppm of Fe, 30 min, 1250 psig hydrogen pressure at ambient conditions, 2 wt % pyrene in hexadecane.

Table 2. Comparison of Dispersion Methods of Iron and Molybdenum Precursors on Their Activity for Pyrene Hydrogenation

Product Distribution (mole %)	Fe Naphthenate		Mo Naphthenate			
	In Situ	Ex Situ	Two Stage	In Situ	Ex Situ	Two Stage
PYR	49.7±1.0	100.0±0.0	94.2±1.0	14.7±1.4	33.3	10.3±1.0
DHP	32.1±0.5	0.0	5.8±1.0	18.7±1.4	32.3	14.3±0.5
THP	2.9±0.1	0.0	0.0	7.5±0.6	9.1	6.2±0.3
HHP	15.4±0.3	0.0	0.0	43.5±0.9	25.5	45.8±0.8
DCHP	0.0	0.0	0.0	15.7±0.7	0.0	23.4±0.8
%HYD	12.0±0.3	0.0	0.8±0.1	34.7±1.7	18.1	40.2±0.6

**Table 3. Comparison of the Activity for the Hydrogenation and Hydrocracking of Naphthalene, 1-Methylnaphthalene, and 2-Hexylnaphthalene**

Product (mole %)				
	No Catalyst	Fe Stearate + S	Fe Naph + S	Mo Naph + S
<b>Naphthalene</b>				
NAP	100.0	85.5±0.4	83.9±0.5	
TET	0.0	14.5±0.4	16.1±0.5	
% HYD	0.0	5.8±0.1	6.4±0.1	
<b>1-Methylnaphthalene</b>				
1-MN	100±0.0	82.3±1.0	81.1±0.6	35.5±0.6
5,6,7,8-1-MN	0.0	11.9±1.0	10.8±0.5	39.2±0.8
1,2,3,4-1-MN	0.0	3.6±0.4	5.3±0.2	25.3±0.9
NAP	0.0	2.2±0.3	2.7±0.4	0.0
% HYD	0.0	6.3±0.4	6.6±0.3	25.8±0.4
<b>2-Hexylnaphthalene</b>				
2-HN	100.0±0.0	70.4±1.2	79.3±0.9	20.1±1.1
2-HT	0.0	16.5±1.2	11.1±0.9	43.5±1.0
2-ET	0.0	13.1±0.9	9.6±0.2	36.4±0.3
%HYD	0.0	14.8±0.7	10.4±0.8	40.0±1.0
%HYC	0.0	13.1±0.9	9.6±0.2	36.4±0.3

Reaction Conditions: 1250 psig H<sub>2</sub> introduced at ambient temperature; 30 minutes, 425°C, S to Fe ratio 3:1, S to Mo ratio 3:1.



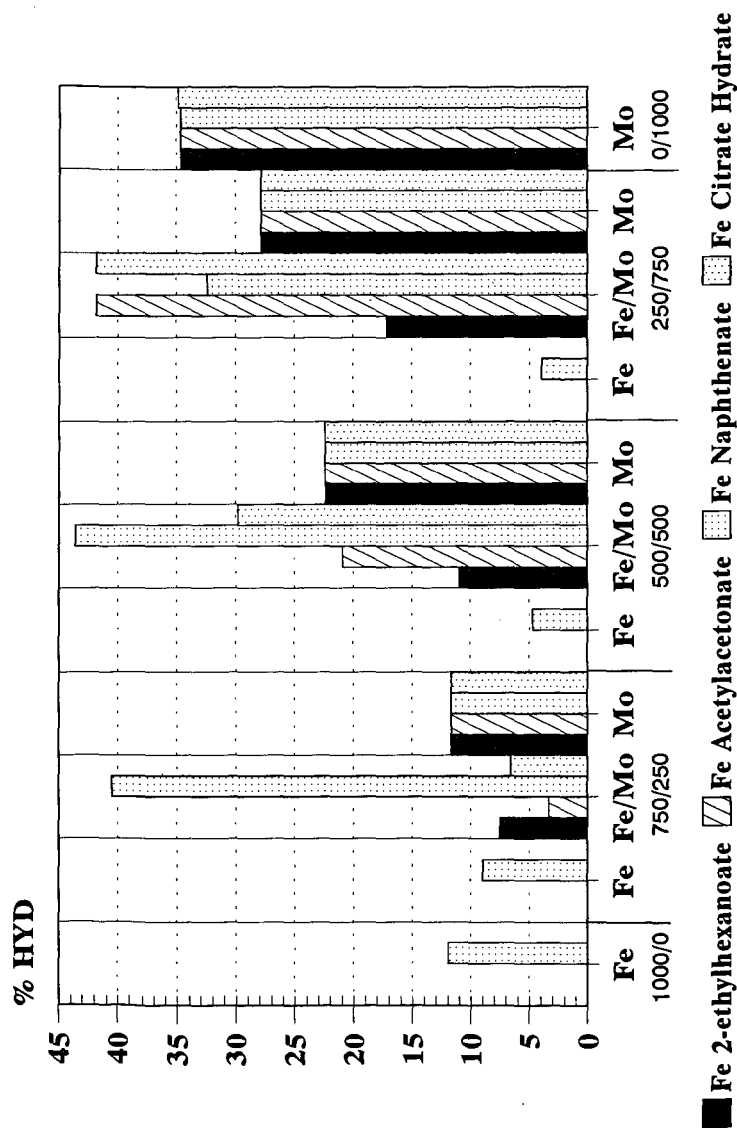


Figure 1. Synergism with Mo Naphthenate.